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Ionized Dopant Concentrations at the Heavily Doped Surface of a Silicon Solar Cell

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National Aeronautics
and Space Administration

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Information Office**

SUMMARY

The metal-oxide-semiconductor (MOS) capacitance-voltage technique is used to determine ionized dopant concentrations at the heavily doped (n^+) surface of a silicon solar cell. These data are combined with concentrations obtained by a bulk measurement method using successive layer removal with measurements of Hall effect and resistivity. From the MOS measurements it is found that N , the ionized dopant concentration, equals $(1.40 \pm 0.1) \times 10^{20} \text{ cm}^{-3}$ at distances between 100 and 220 nm from the n^+ surface. The bulk measurement technique yields average values of N over layers whose thickness is 2000 nm. Assuming a linear concentration variation near the surface; the combined data indicate that the ionized dopant concentration is constant from the surface to a depth of 2000 nm. These results show that, at the high concentrations encountered at the n^+ surface, the MOS capacitance-voltage technique, when combined with a bulk measurement method, can be used to evaluate the effects of materials preparation methodologies on the surface and near surface charge concentrations of silicon solar cells.

INTRODUCTION

It has been proposed that increased silicon solar-cell efficiencies can be attained by controlling surface concentrations and impurity profiles in the heavily doped, surface region (refs. 1 and 2). To achieve this, it is necessary to employ diagnostic techniques that can directly evaluate the effects of specific materials preparation methodologies on surface and near surface concentrations. At present such techniques as secondary ion mass spectroscopy (SIMS, ref. 3) and successive layer removal (SLR, ref. 4) are used to obtain dopant profiles in the heavily doped n^+ region of n^+p silicon solar cells. However, in addition to being destructive, the aforementioned techniques have insufficient resolution to allow determination of concentrations closer than approximately 1000 nm from the surface. On the other hand, the metal-oxide-semiconductor (MOS) capacitance-voltage technique yields numerical results for ionized dopant concentrations within 100 nm of the n^+ surface and the charge density in surface and oxide states at the oxide-semiconductor interface (ref. 5); furthermore, this technique is nondestructive. In the present study the MOS capacitance-voltage method was combined with a bulk profiling technique to yield more complete concen-

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tration data than is obtainable with either measurement alone. Specifically, solar cell, MOS capacitance-voltage measurements are combined with bulk concentrations obtained by an SLR technique utilizing measurements of sheet resistivity and Hall effect (ref. 4). At the high dopant concentrations encountered near the n^+ surface, the MOS capacitance-voltage technique determines concentrations much closer to the silicon surface than does the SLR method. Hence, combination of the two methods should result in data extending from within the bulk of the n^+ region up to and including the heavily doped silicon surface.

THEORY

In this section the relations used to obtain ionized impurity concentrations are detailed for both methods. In addition to obtaining bulk impurity concentrations at the silicon surface, the MOS capacitance-voltage technique can be used to measure the density of charge in oxide and surface states at the oxide - silicon interface (ref. 5). However, in the present case, the intent is to show that the MOS capacitance-voltage measurement can extend the results of a bulk measurement technique to the solar-cell's silicon surface. Hence, we consider only the determination of impurity concentration in the vicinity of the silicon surface.

Concentrations by MOS Capacitance-Voltage Measurements

The method used in obtaining N , the ionized dopant concentration, at a distance Z from the solar-cell's silicon surface follows the original detailed exposition given in reference 5. The standard MOS capacitor is shown in figure 1, and the high-frequency-equivalent circuit of the standard MOS capacitor (ref. 6), in figure 2. In the figures C_o is the oxide capacitance, while C_{sc} is the capacitance of the semiconductor space-charge layer. Application of a varying dc voltage across terminals X-X causes C_{sc} to vary, and thus the total high-frequency capacitance C_{hf} , where

$$C_{hf} = \frac{C_o C_{sc}}{C_o + C_{sc}} \quad (1)$$

The ionized impurity concentration at a depth Z is determined from the (refs. 7 and 8)

$$N = \frac{2}{q\epsilon A^2 \frac{[d(1/C_{hf}^2)]}{dV}} \quad (2)$$

where q is the electronic charge, ϵ is the dielectric permittivity of the semiconductor, A is area of the MOS capacitor, and V the voltage applied across terminals X-X in figure 1.

In the solar cell MOS device shown in figure 3 (ref. 5), the metal plate of the MOS capacitor is deposited on the tantalum oxide, solar-cell antireflection coating. Thus, the solar-cell antireflection coating is also the oxide in the MOS device. The remaining connection to the MOS capacitor is made to the metal solar-cell front surface contact fingers, as shown. This configuration was chosen to avoid the complicating effects of the p-n junction. Its use as an MOS capacitor was introduced and experimentally and theoretically justified in reference 5. The equivalent circuit of the solar-cell - MOS configuration is shown in figure 4, where the oxide losses are represented by the resistance R_o and the semiconductor losses by R_s . To obtain numerical values of C_{hf} from equation (1), and hence N from equation (2), C_{sc} and C_o must be obtained from the capacitance-voltage data. However, in the solar cell case, one measures a capacitance C_M , which, according to the equivalent circuit of figure 4, is given by (ref. 5)

$$C_M = \frac{C_{sc} [1 + (\omega R_o)^2 C_o (C_{sc} + C_o)]}{(1 - \omega^2 C_{sc} C_o R_o R_s)^2 + [\omega C_{sc} (R_o + R_s) + \omega C_o R_o]^2} \quad (3)$$

Since C_M is measured directly using the configuration of figure 3, C_{sc} can be obtained from equation (3) if C_o , R_o , and R_s are known. The parameters C_o and R_o are properties of the oxide, and the method used in their numerical evaluation involves measurement on the simple MOS device of figure 1. Further details for measuring these quantities are given in later sections of this report. To obtain R_s , use is made of the fact that at sufficiently high applied dc voltage the semiconductor space-charge region is in the strong accumulation condition (ref. 6). For an n-type semiconductor this implies a very high electron concentration near the surface, and C_{sc} is effectively shorted out with its capacitance value approaching infinity (ref. 9). This condition will occur at C_{max} , the maximum value of C_M . From the equivalent circuit of figure 4, one obtains (ref. 5)

$$C_{\max} = \frac{C_o R_o^2}{(R_o + R_s)^2 + (\omega C_o R_s R_o)^2} \quad (4)$$

Knowing C_{\max} , R_o , and C_o allows the calculation of R_s from the preceding relation. Hence, using C_M , the measured capacitance C_{sc} is obtained from equation (3) at different applied voltages V , and N is obtained from equation (2). In addition, having numerical values for C_{sc} allows Z , the distance from the surface at which N is evaluated, to be obtained from the relation (refs. 7 and 8)

$$Z = \frac{\epsilon A}{C_{sc}} \quad (5)$$

Concentration by Successive Layer Removal Technique

In the successive layer removal (SLR) technique, layers in the heavily doped region of the solar cell are progressively removed by etching. Hall coefficients and resistivity are measured before and after each layer is removed, and the ionized dopant concentrations found using the following relations (refs. 4, 10 and 11):

$$\Delta \left(\frac{R_{HS}}{\rho_S^2} \right) = qN(Z)\mu^2(Z)\Delta Z \quad (6)$$

$$\Delta \left(\frac{1}{\rho_S} \right) = qN(Z)\mu(Z)\Delta Z \quad (7)$$

where R_{HS} and ρ_S are sheet Hall coefficient and resistivity, respectively, and $\Delta(R_{HS}/\rho_S^2)$ and $\Delta(1/\rho_S)$ are the changes measured in the quantities after removal of a layer whose mean distance from the surface is Z ; q is the electronic charge; $N(Z)$ and $\mu(Z)$ are averages of the concentration and mobility, respectively, of the slice centered at Z ; Z is the distance from the solar-cell surface to the center of the slice; and ΔZ is the layer thickness. The sheet resistivities and Hall coefficients are measured using a method developed by van der Pauw (ref. 12) for making Hall effect and resistivity measurements on arbitrarily shaped samples of uniform thickness with electrical contacts made to the sample periphery. To illustrate the method, consider a disk with contact made to its periphery as shown by the arrows in figure 5. To determine R_{HS} , the sheet Hall coefficient, a magnetic field is applied perpendicular to

the face of the disk. An external power source is connected to contacts 1 and 3 such that the current I_{13} flows through the disk between these contacts. The Hall voltage V_{24} is measured across contacts 2 and 4, and the sheet Hall coefficient determined by the relation (refs. 11 and 12)

$$R_{HS} = \frac{10^8 V_{24}}{I_{13} B} \quad \text{cm}^2/\text{C} \quad (8)$$

where voltage is measured in volts, current in amperes, and B , the magnetic field, is measured in gauss. (The factor 10^8 appears in the numerator because B , which is measured in G must be multiplied by 10^{-8} , in the denominator, to convert from G to Wb/cm^2 .) To determine the sheet resistivity ρ_S , a current I_{12} is caused to flow between the contacts 1 and 2, and the voltage V_{34} is measured between points 3 and 4. The sheet resistivity is then given by (refs. 4 and (11))

$$\rho_S = \left(\frac{\pi}{\ln 2} \right) \frac{V_{34}}{I_{12}} \quad \Omega/\text{square} \quad (9)$$

As layers of known thickness, ΔZ are etched away from the heavily doped cell surface, ρ_S and R_S are determined before and after successive layer removal, and the ionized dopant concentrations determined for each layer. This method yields an average value of concentration for $N(Z)$ over a slice of thickness ΔZ .

EXPERIMENTAL PROCEDURE

The methods used in sample preparation and the measurements performed are outlined in figure 6. The starting material was a 10-ohm·cm, p-type, 2- by 2-cm, silicon wafer of 280 μm thickness. The wafer was heated at 848^o C for 30 minutes in phosphorous oxytrichloride, thus forming the solar-cell n^+p junction by diffusion. The diffused wafer was then cleaved into two 1- by 2-cm wafers for use in the two types of measurement. The wafer for use in the MOS capacitance-voltage measurements was processed into a solar cell by vacuum deposition of silver-aluminum front and back contacts and a front surface tantalum oxide antireflection coating. The antireflection coating was deposited by electron-beam evaporation to a thickness of 6400 nm. The MOS capacitor was then completed by vacuum depositing a circular gold dot between the front contact fingers (fig. 13). The diameter of the dot was 2.54×10^{-2} cm, and its thickness was approximately 0.5 μm . A varying dc voltage was then applied between the metal dot and the front contact fingers, and the capacitance was measured between these two points with a Boonton model 71AR capacitance meter operating at a frequency

of 1 MHz. The output of the capacitance meter was displayed on the vertical axis of an x-y recorder, and the applied dc voltage was displayed on the horizontal axis.

To obtain the numerical values of C_0 and R_0 , a simple MOS device (fig. 1) was fabricated at the same time as the solar-cell MOS device. The semiconductor was a 2- by 2-cm wafer of 0.02-ohm-cm, n-type silicon, the Ta_2O_5 being deposited on the wafer at the same time that the oxide was deposited on the solar-cell - MOS device. During oxide deposition, the silicon wafer was positioned alongside the solar cell. The simple MOS device was then completed by deposition of a gold dot whose dimensions were the same as that deposited for the solar-cell - MOS device. Measurements on the simple MOS device were then performed using a Boonton model 75A capacitance-conductance bridge whose operating frequency was 1 MHz.

The SLR measurements were carried out on the second 1- by 2-cm wafer using the configuration shown in figure 7. The circular pattern shown was formed on the n^+ surface by a photoresist technique and then etched to a depth of approximately 10 μm using a 4:3:2 solution of nitric, acetic, and hydrofluoric acids. The shaded portions are regions where the silicon has been etched away. The resultant mesa is in the form of a disk with electrical contacts made at its periphery by the remaining silicon (areas marked 1 to 4 in fig. 7). Thus, the etched mesa of figure 7 corresponds to the disk of figure 5. Successive layers are removed in 2000 nm steps by anodic oxidation and etching in hydrofluoric acid (ref. 10). Sheet resistivities ρ_S and sheet Hall coefficient R_{HS} are measured before and after the removal of each layer. Equations (6) to (9) were used to determine the bulk concentrations at various distances from the original heavily doped silicon surface. As mentioned previously, the SLR method yields average values of concentration for each layer, Z being taken as the depth corresponding to the center of each slice.

RESULTS

The solar-cell capacitance-voltage data are shown in figure 8, where, because of dielectric breakdown, the applied dc voltage is limited to 20 volts. To obtain values of C_0 and R_0 for use in equations (1) and (3), we use the results of the measurements carried out on the simple MOS device whose vacuum deposited oxide (Ta_2O_5) is also the oxide coating of the solar cell. The capacitance-voltage data for the simple MOS device are shown in figure 9 where strong accumulation (ref. 6) occurs for voltages greater than 0.5 volt. In strong accumulation the space-charge capacitance is effectively shorted out (ref. 9), and the simple MOS device becomes a two-plate capacitor whose capacitance is C_0 , and the reciprocal of conductance is equal to R_0 . The conductance-voltage data for the simple MOS device are shown in figure 10, where

strong accumulation occurs for voltages greater than 0.5 volt. From these measurements it is found that $C_o = 1.95 \times 10^{-10}$ F and $R_o = 2 \times 10^3 \Omega$. Hence, from equation (4), with $C_{\max} = 1.32 \times 10^{-10}$ F, it is found that $R_s = 310 \Omega$. Using equation (3), C_{sc} can now be evaluated from measured values of C_M and C_{hf} can be calculated from equation (1) over the voltage range shown in figure 8.

A plot of $1/C_{hf}^2$ as a function of applied voltage is presented in figure 11. It will be shown in the discussion section that the MOS capacitance-voltage data, in the present case, can only yield valid numerical values for concentrations at distances between 100 and 220 nm from the n^+ surface. The dc voltages corresponding to these distances are indicated by the dashed lines in figure 11, which shows that the range of validity corresponds approximately to the linear portion of the $1/C_{hf}^2$ plot. From the slope of the linear portion of figure 11 and using equation (2), it is found that $N = 1.4 \times 10^{20} \text{ cm}^{-3}$. This represents an average value over the interval between approximately 100 and 220 nm. Discrete values of N can be obtained over this interval by determining the slope between data points in figure 11 and again using equation (2). The results are shown in figure 12 from which it is found that $N = (1.4 \pm 0.1) \times 10^{20} \text{ cm}^{-3}$ over the depth interval between 100 and 220 nm from the surface. The limiting distance from the surface for which the preceding value of N applies is close enough to the surface so that N is considered to be a surface parameter.

The importance of silicon surface concentration in determining solar-cell performance has been postulated in reference 2. However, the postulate is based on calculations, there being no direct measurement of surface concentrations as related to solar-cell efficiencies. In this respect the MOS capacitance-voltage technique can be used to measure surface concentrations and is thus an important tool in attempts to increase solar-cell efficiency through variation of surface concentration at the n^+ surface of silicon solar cells (ref. 2).

The SLR data are shown in figure 13, together with the value of N obtained by the MOS capacitance-voltage method. From the SLR data the average value of N over the first 2000-nm slice is $(1.3 \pm 0.2) \times 10^{20} \text{ cm}^{-3}$. This agrees, within experimental error, with the value of N obtained from the MOS data. Hence, assuming a linear concentration variation near the surface, the combined data indicate a constant ionized dopant concentration to a depth of 2000 nm from the surface.

DISCUSSION

Considering the MOS measurements, equations (2) and (5) are valid when the semiconductor space-charge region is in the depletion condition (refs. 7 and 8). For an n-type semiconductor the charge in the depleted space-charge region is assumed to

be due solely to ionized donors. From this it can be shown (ref. 6) that Z_{\max} , the maximum distance of the depletion region from the semiconductor surface, is given by

$$Z_{\max} = \sqrt{\frac{2\epsilon(E_F - E_i)}{qN}} \quad (10)$$

where N , as before, is the ionized donor concentration in the depletion layer and E_F and E_i are the energies of the Fermi and intrinsic energy levels, respectively. The effects of heavy doping (ref. 13) are included in equation (10) when computing the quantity $(E_F - E_i)$. Thus, with $(E_F - E_i) = 0.51$ eV (ref. 13), $\epsilon = 1.06 \times 10^{-12}$ F/cm, and $N = 1.4 \times 10^{20} \text{ cm}^{-3}$, it is found that $Z_{\max} \approx 220$ nm. This is the maximum distance from the n^+ surface for which N can validly be obtained from equation (2) using the present measurement technique.

There is also a limiting minimum value Z_{\min} , which arises from the breakdown of the depletion approximation (refs. 14 and 15). This limitation occurs because of the breakdown of the depletion approximation as the applied voltage changes and the depth of the depletion region becomes smaller. For this case the surface potential decreases, and majority carriers (electrons) begin to enter the depletion region. Thus, the electrical charge in the depletion region is no longer due to ionized donors (refs. 14 and 15) and

$$Z_{\min} = 2 \sqrt{\frac{2kT\epsilon}{q^2N}} \quad (11)$$

Hence, with $T = 300$ K, $Z_{\min} \approx 100$ nm. Thus the limits to which the MOS capacitance-voltage data can, in the present case, yield reliable values of N lie between 100 and 220 nm.

The variation of Z_{\min} and Z_{\max} with concentration can be calculated from equations (10) and (11). These calculations have been carried out as part of the present study. The results are shown in figure 14 for N varying from 10^{21} to 10^{14} cm^{-3} . It is seen that Z_{\min} , the distance of closest approach, becomes very small at concentrations typical of current silicon solar cells (10^{20} cm^{-3}).

As mentioned previously, the limitation on Z_{\min} arises because of the presence of majority carriers in the depletion region. In this respect, experimental and theoretical techniques exist for extending the MOS capacitance-voltage measurements to the surface for all ionized donor concentrations (ref. 16). However, the aforementioned techniques (ref. 16) are of greater complexity than those used in the present case. Furthermore, for the heavily doped solar-cell surface the MOS capacitance-voltage technique used in the present study is more than adequate.

The distance from the surface Z at which the MOS technique determines surface concentration is much closer than that obtainable with the SLR method. In fact, one can only use the latter method to determine an average value over the removed larger thickness. In this respect, layers with thicknesses as low as 1000 nm have been removed in the SLR measurements (ref. 17). The SIMS method, another commonly used profiling technique, determines concentrations at distances equal to or greater than 1000 nm from the semiconductor surface (ref. 3). Hence, at high concentrations, the MOS capacitance-voltage technique yields measurements closer to the surface than either the SIMS or SLR methods. In addition, the MOS capacitance-voltage method is nondestructive while the SLR and SIMS methods are destructive.

CONCLUDING REMARKS

The MOS capacitance-voltage method, when combined with a bulk profiling technique, yields more complete data than are obtainable with either measurement alone. In particular, at the high concentrations encountered on the heavily doped surface of silicon solar cells, the MOS capacitance-voltage technique yields ionized dopant concentrations close enough to the surface to be considered a surface parameter. Hence, it has been successfully demonstrated that the MOS capacitance-voltage method can be used as a diagnostic tool in evaluating the effects of specific materials preparation methodologies on the surface and near surface concentrations of silicon solar cells. These direct measurements of surface concentrations will be highly significant in any experimental program aimed at evaluating the theoretical predictions relating solar-cell performance to surface concentrations.

SUMMARY OF RESULTS

The MOS capacitance-voltage method has been used to nondestructively measure N , the ionized dopant concentration near the heavily doped surface of an n^+p silicon solar cell. The MOS measurements yield the value $N = (1.4 \pm 0.1) \times 10^{20} \text{ cm}^{-3}$ at depths between 100 and 220 nm from the surface. Calculations based on breakdown of the depletion approximation show that at these high dopant concentrations measurements of N by the currently used MOS method are valid only between 100 and 220 nm from the n^+ surface. Measurements extending further into the bulk of the n^+ region are carried out using a destructive successive layer removal (SLR) technique, combined with Hall effect and resistance measurements, which yields average values of N over successive 2000-nm layers. The average value of N obtained by the SLR method for the first 2000-nm layer is $(1.30 \pm 0.2) \times 10^{20} \text{ cm}^{-3}$, which is in agreement with the near-

surface value obtained by the MOS method. Assuming a linear variation of concentration with depth close to the n^+ surface, the combined results yield a constant value for the ionized dopant concentration at depths up to 2000 nm from the n^+ surface. These results demonstrate that the nondestructive MOS capacitance-voltage method can be used to extend, up to the n^+ surface, measurements of the ionized dopant concentration obtained within the bulk of the n^+ region by a destructive bulk measurement technique, such as the SLR method.

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National Aeronautics and Space Administration,
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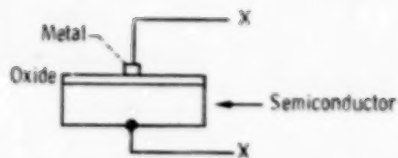


Figure 1. - Simple MOS device. The dc voltage is applied and capacitance measured across terminals X-X.

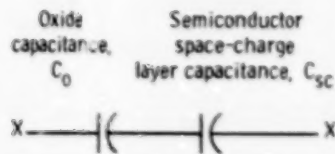


Figure 2. - High frequency equivalent circuit of MOS device shown in figure 1.

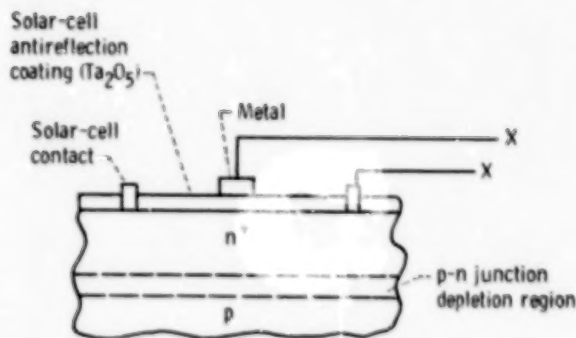


Figure 3. - Solar-cell MOS configuration. The dc voltage is applied, and capacitance measured across terminal X-X.

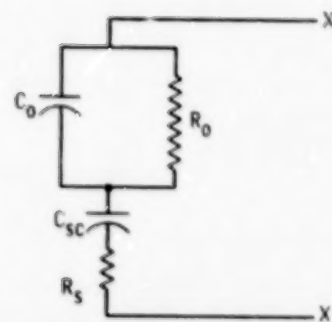


Figure 4. - High-frequency equivalent circuit of solar-cell MOS configuration.

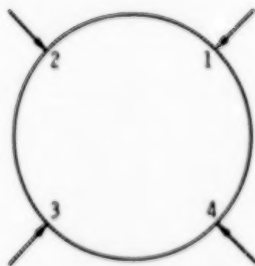


Figure 5. - Cylindrical disk with electrical contacts (arrows) at periphery. The figure illustrates method for determining resistivity and Hall coefficient for use in equations (6) and (7).

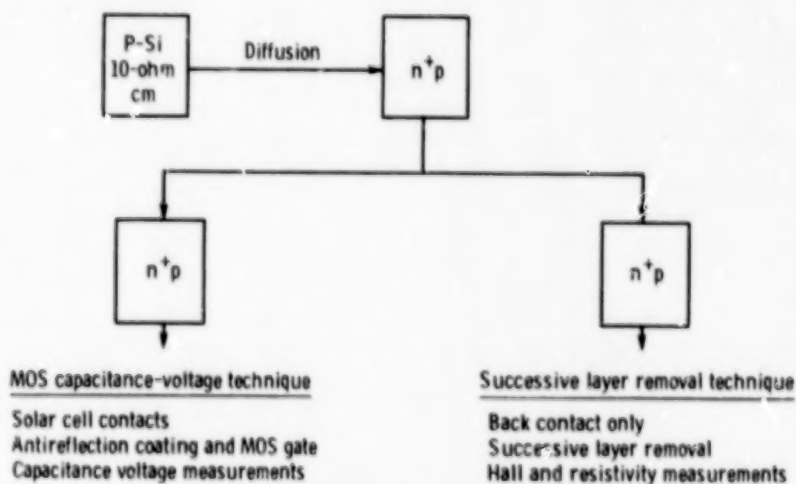


Figure 6. - Sample preparation and measurement techniques.

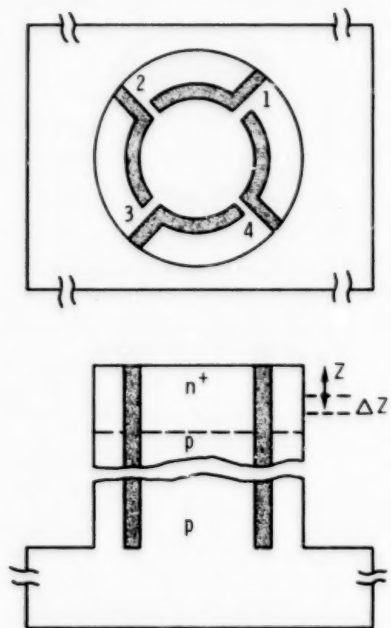


Figure 7. - Etched mesa used in determining concentrations by the successive layer removal (SLR) technique. The shaded portions are regions where the silicon has been etched away.

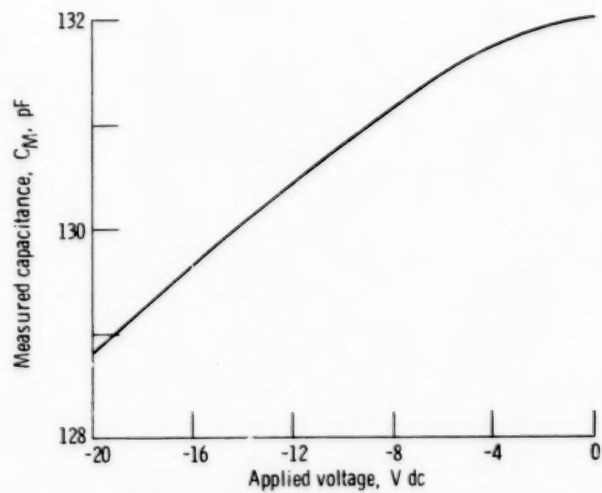


Figure 8. - Solar cell MOS capacitance-voltage curve.

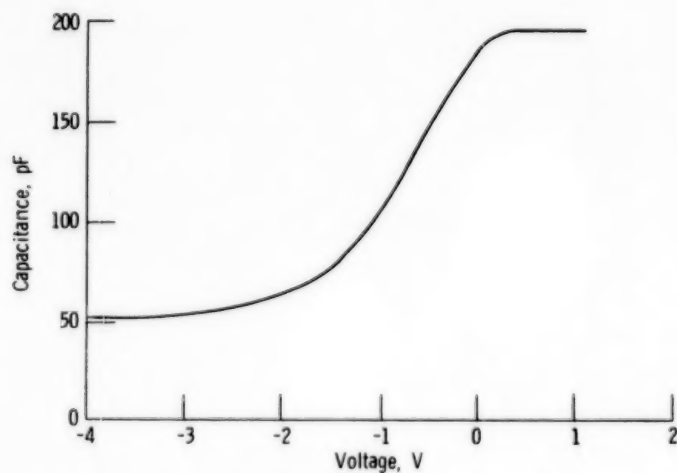


Figure 9. - Capacitance-voltage data for simple MOS device.

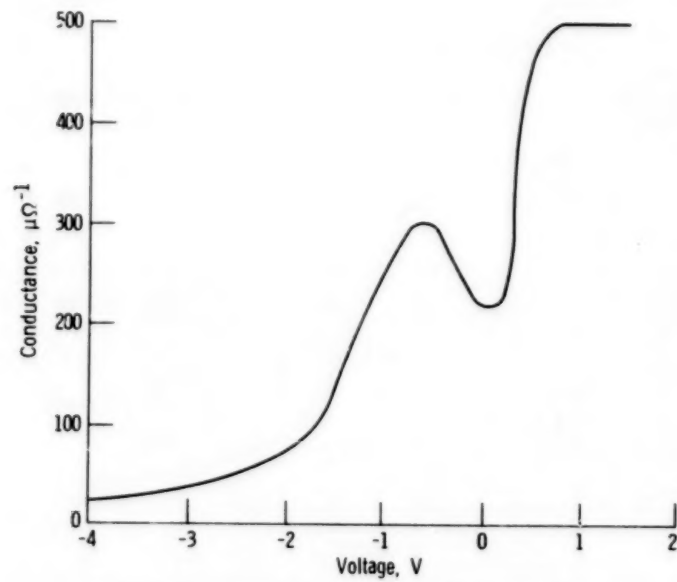


Figure 10. - Conductance-voltage data for simple MOS device.

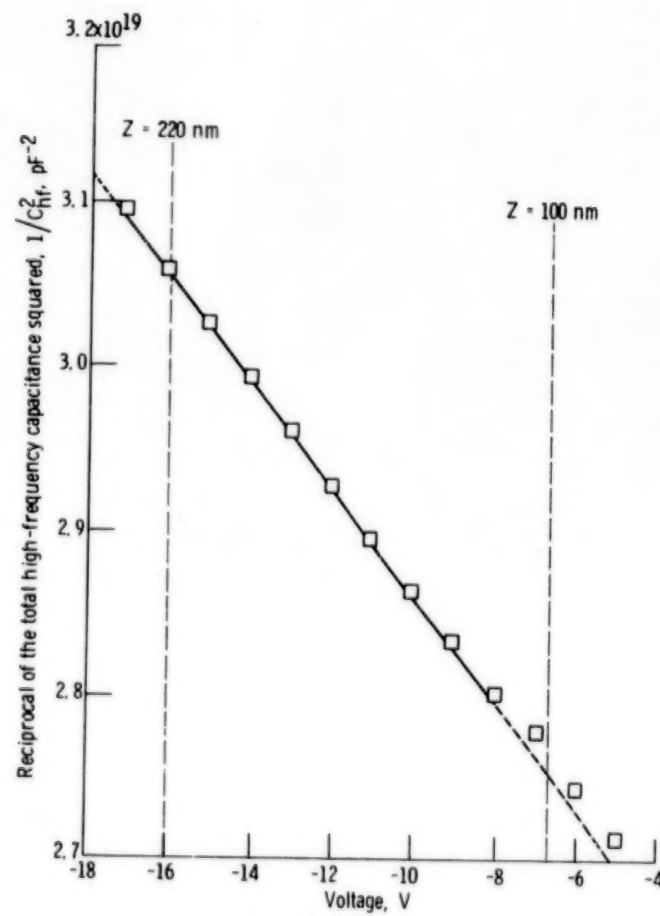


Figure 11. - $1/C_{hf}^2$ versus applied dc voltage.

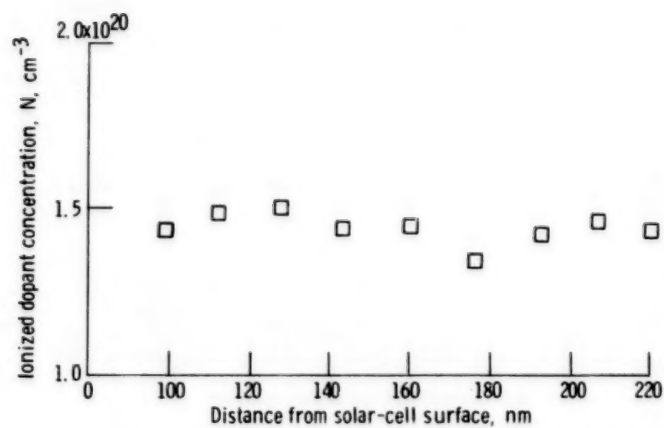


Figure 12. - Ionized impurity concentrations near the n^+ surface.

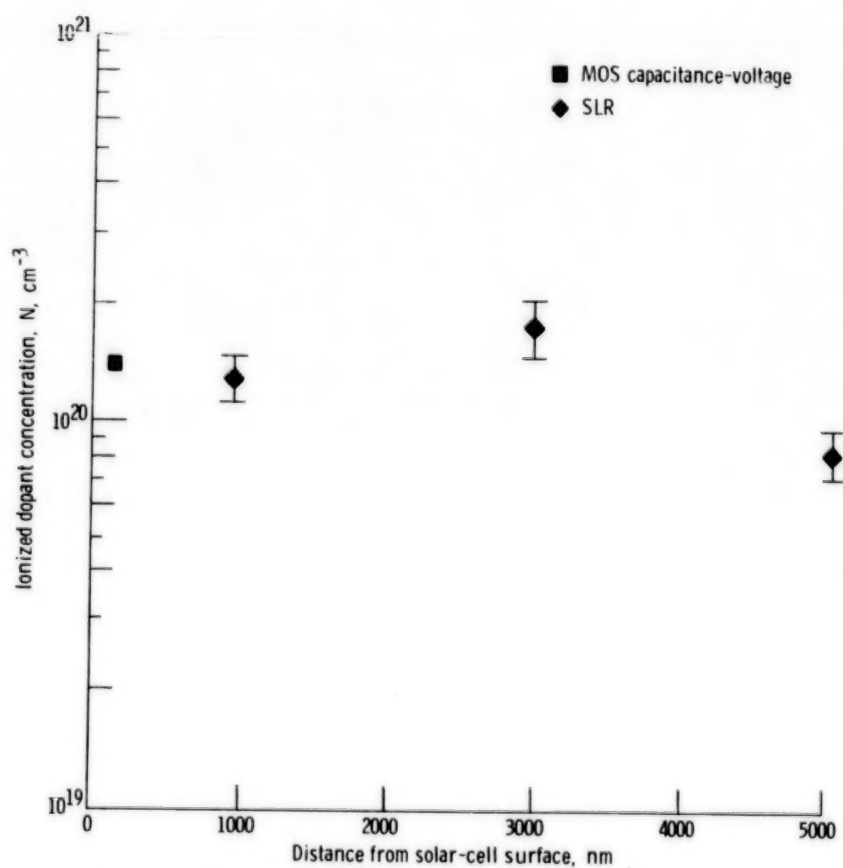


Figure 13. - Concentrations at specific distances from solar-cell surface as obtained by the MOS capacitance voltage and SLR methods.

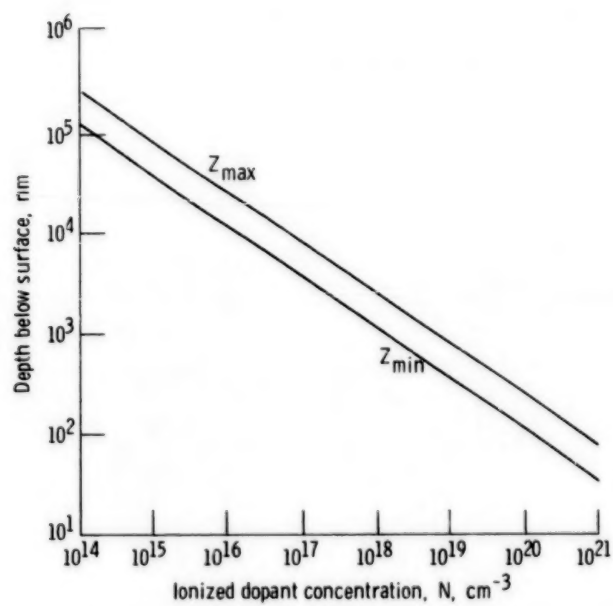


Figure 14. - Maximum and minimum distances from surface for which these MOS capacitance-voltage measurements are valid in determination of ionized dopant concentration.

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16. Abstract <p>The metal-oxide-semiconductor (MOS) capacitance-voltage technique is used to determine ionized dopant concentrations at the heavily doped (n^+) surface of a silicon solar cell. These data are combined with concentrations obtained by a bulk measurement method using successive layer removal with measurements of Hall effect and resistivity. From the MOS measurements it is found that the ionized dopant concentration N has the value $(1.4 \pm 0.1) \times 10^{20} \text{ cm}^{-3}$ at distances between 100 and 220 nm from the n^+ surface. The bulk measurement technique yields average values of N over layers whose thickness is 2000 nm. Assuming a linear concentration variation near the surface, the combined data indicate that the ionized dopant concentration is constant from the surface to a depth of 2000 nm. These results show that, at the high concentrations encountered at the n^+ surface, the MOS C-V technique, when combined with a bulk measurement method, can be used to evaluate the effects of materials preparation methodologies on the surface and near surface charge concentrations of silicon solar cells.</p>					
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